The ways to improve the energy conversion efficiency in erbium-doped Gd_2O_3 nanoparticles

The ways to improve the energy conversion efficiency in erbium-doped Gd_2O_3 nanoparticles

Yu A Kuznetsova[1], **A F Zatsepin**[1], **M A Mashkovtsev**[1], **V N Rychkov**[1], **S P Vyatkina**[1]
[1]Institute of Physics and Technology, Ural Federal University, Ekaterinburg, Russia

Abstract. The basic requirements for the crystal lattice and defectiveness of Gd_2O_3 matrix as well as for the concentration of Er^{3+} dopants to achieve the enhanced parameters of energy conversion in Gd_2O_3:Er nanoparticles are summarized. The obtained data allow to optimize and improve the functional characteristics of Gd_2O_3:Er -based down-conversion layers applying in solar cells.

1. Introduction

Gadolinium oxide doped with rare-earth ions are of interest as a new type of material for energy conversion devices, in particular, for solar cells [1-3]. Improvement of functional characteristics of convertors based on rare-earths requires the optimization of synthesis technologies which determine the atomic and electronic structure of materials and, ultimately, their optical properties. In present work, we summarize the basic requirements for the crystal structure type and defectiveness of Gd_2O_3 matrix as well as the concentration of dopant ions to achieve the enhanced energy conversion efficiency.

2. Samples and Methods

The pure and erbium-doped Gd_2O_3 nanoparticles with a cubic crystal lattice were synthesized by chemical precipitation from water-alcohol solutions of gadolinium and erbium nitrates with the obtaining of layered rare-earth hydroxides as intermediate products. The method of self-propagating high-temperature combustion with glycine and ammonium nitrate as fuels was used for obtaining the monoclinic modification of Gd_2O_3 nanoparticles. XRD, SEM and Raman spectroscopy data confirmed that the chosen technologies of synthesis provide the obtaining of stable low-dimensional monophasic erbium-doped gadolinium oxide with an average particle size of 50 nm.

Optical properties of cubic and monoclinic nano-Gd_2O_3:Er polymorphs were investigated in a 8-300 K temperature range by using a McPherson VuVAS spectrometer and Perkin Elmer LS 55 spectrophotometer.

3. Results

3.1 Requirements for Gd_2O_3 matrix

Experimental and theoretical study of gadolinium oxide electronic structure by X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations revealed intrinsic point defects caused by the technological features of synthesis for nanoparticles with cubic and monoclinic crystal structures [4]. In cubic polymorph, there is a violation of oxygen coordination of lattice cations (oxygen vacancies). Photoluminescence optical spectroscopy data combined with the thermoluminescence measurements indicated three types of oxygen-deficient centers with different

charge states: F^{2+}, F^{+} and F – centers [5]. Non-elementary luminescence in 2.0 – 3.5 eV spectral range observed for cubic phase of nano-Gd_2O_3 is formed by radiative transitions in different types of oxygen vacancies. For the monoclinic nano-Gd_2O_3 phase no optical activity was detected even at helium temperature. The reason for this, as XPS and DFT data indicate, is presence of impurity hydroxide ions that have emerged from the precursors used in the synthesis. OH^- – groups are external quenchers of luminescence due to an increase in the probability of non-radiative deactivation of excited states of emission centers [4]. Thereby, the monoclinic polymorph is not suitable for energy conversion purposes and we focus on Gd_2O_3 nanoparticles with a cubic structure.

Figure 1 shows the photoluminescence (PL) and PL excitation spectra for cubic nano-Gd_2O_3 doped with erbium ions. The main feature is the presence of bands corresponding to the transitions in Gd^{3+} ions, that is not typical for regular cations of host lattice. Cations in regular lattice positions form extended states of conduction band, so there are no any local states of Gd^{3+} ions in the ideal Gd_2O_3 lattice. An existence of Gd^{3+} local electronic levels in the optical transparence area of Gd_2O_3 host-matrix indicates that these ions have distorted energy structure. It is reasonable explained by influence of oxygen defects in the nearest environment of Gd^{3+} ions, which are responsible for the change in the cation energy structure and the appearance of additional Gd^{3+} electronic states in the Gd_2O_3 band gap region. By this way, the Gd^{3+} ions become optically active and can be excited in the UV spectral region with the following energy transfer to the erbium dopants. This provides an additional channel for energy conversion and one of the main advantages of Gd_2O_3:Er system, because there is no need to introduce into the matrix the ions acting as donors of excitation, since this role is played by host lattice cations – Gd^{3+} ions. Down-conversion in Gd^{3+} – Er^{3+} pair is especially promising for solar energy applications. It can provide a reduction in thermalization losses that occur in a silicon solar cell when absorbing photons with an energy exceeding the Si band gap. In other words, additional quanta with UV energy will participate in the solar energy conversion [1-3].

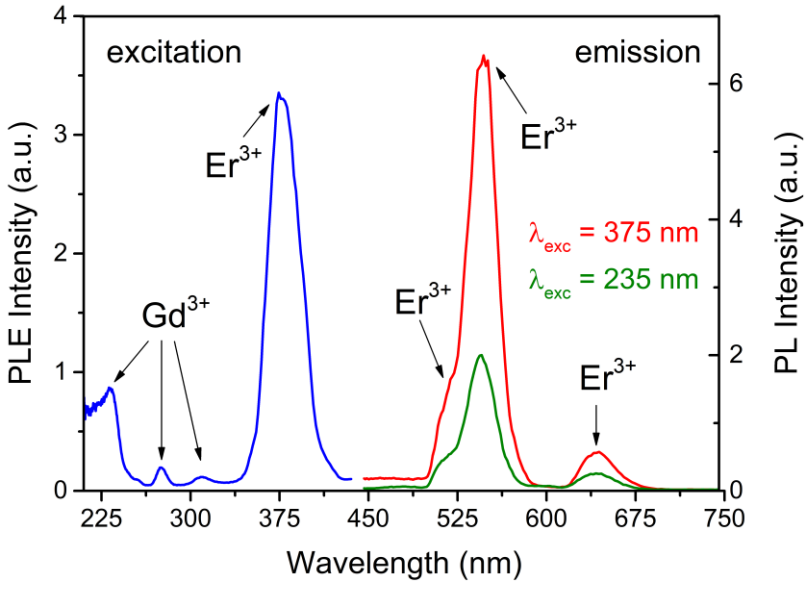

Figure 1. Photoluminescence (red and green lines, right scale) and excitation (blue line, left scale) spectra for Gd_2O_3:Er nanoparticles at room temperature. Arrows show the optical transitions in Gd^{3+} and Er^{3+} ions.

3.2 Requirements for Er^{3+} concentration

After determining the matrix characteristics, the next task is to find the optimal concentration of dopant. On the one hand, with an increase in the Er^{3+} concentration, the efficiency and the rate of $Gd^{3+} \rightarrow Er^{3+}$ energy transfer also increase due to a shortening of donor-acceptor distance. However, at a high amount of acceptor the non-radiative energy migration along the Er^{3+} ions can occur (concentration quenching), which leads to a decrease in quantum efficiency [6]. Thus, it is necessary to determine such Er^{3+} concentration, that will provide a high overall efficiency of energy conversion.

We have considered this problem by analyzing the temperature dependences of luminescence for Gd_2O_3 nanoparticles with different Er^{3+} concentration (from 0.25 to 8%).

Monitoring changes in the luminescence properties of Gd_2O_3:Er nanoparticles in temperature range of 8-300 K we found that quenching curves for Er^{3+} emission don't obey the classic Mott law and the low-temperature plateau is absent in the $I(T)$ dependences. It means the activation energy for emission quenching for Er^{3+} centers in Gd_2O_3 nanoparticles takes a dispersed rather than a discrete value. The dispersion of optical centers over the energy barrier for luminescence quenching was represented by a Gaussian with different parameters for different Er^{3+} concentrations. A detailed analysis of quenching curves is described in our work [7]. The largest values of width and maximum of the distribution were found for Gd_2O_3:Er (1%) nanoparticles. This means that for a given activator concentration, one can expect the least non-radiative losses. It is confirmed also by the phenomenon of giant phonon softening found by independent measurements of the reflection spectra for nano-Gd_2O_3:Er, where namely for Gd_2O_3:Er (1%) sample the smallest frequency of lattice vibrations was detected [8]. We performed a quantitative estimation of quantum efficiency of luminescence for all samples of the concentration series Gd_2O_3:Er (0.25-8%), following the equation that accounts the dispersion of energy barrier for luminescence quenching:

$$\eta = \frac{1}{1 + \int_0^\infty \exp(-E_a/kT) g(E_a) dE_a}, \quad (1)$$

where η is the quantum efficiency, E_a is the activation energy for emission quenching, $g(E_a)$ is the Gaussian distribution of optical centers over the E_a and k is the Boltzmann constant. The obtained quantum efficiency values as a function of Er^{3+} concentration are shown in figure 2. Indeed, for Gd_2O_3:Er (1%) nanoparticles there is enhanced quantum efficiency of erbium luminescence under UV radiation conversion due to the minimization of thermal losses. The basic requirements for Gd_2O_3 matrix and Er^{3+} dopant for achieving the improved characteristics of energy conversion as well as the main optical parameters of Gd_2O_3:Er system are summarized in table 1.

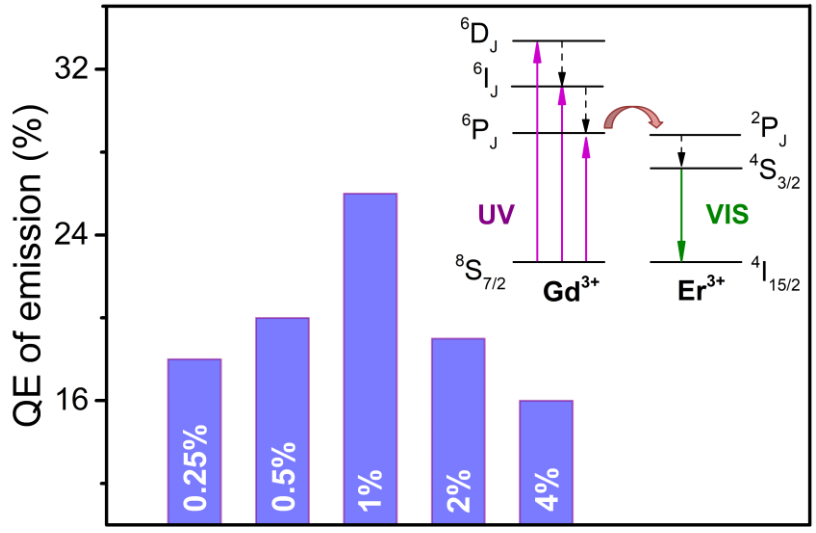

Figure 2. Quantum efficiency (QE) of erbium visible emission under UV radiation conversion due to the $Gd^{3+} \rightarrow Er^{3+}$ energy transfer in Gd_2O_3 nanoparticles doped with 0.25-4% of Er^{3+} ions.

Table 1. Structural and optical parameters of Gd_2O_3:Er nanoparticles for achieving the improved efficiency of UV-visible conversion.

Fundamental characteristics		*Tunable parameters*	
Crystal structure	cubic Ia-3 [4]	Er^{3+} concentration	1% [7]
Lattice parameter	10.81 Å [2]	$Gd^{3+}\rightarrow Er^{3+}$ energy transfer efficiency	50% [2]
Direct energy gap	5.38 eV [8]	$Gd^{3+}\rightarrow Er^{3+}$ energy transfer rate	29 μs [7]
Indirect energy gap	5.15 eV [8]	Quantum efficiency of emission	26% [7]
Phonon frequency	242 cm^{-1} [8]	Decay time of emission	86 μs [7]

4. Conclusion

Summarizing the data about atomic structure, electronic states and optical properties of Gd_2O_3:Er nanoparticles we established the basic requirements for matrix and activator to achieve improved characteristics of UV-visible energy conversion. The cubic structure of Gd_2O_3 host lattice is more preferable than the monoclinic phase due to the presence of optically active defective Gd^{3+} cations acting as excitation donors and providing an additional channel for UV radiation conversion. Monoclinic structure of Gd_2O_3 nanoparticles is not suitable for application as a luminescent material because of impurity hydroxide ions that arise at the synthesis stage and completely quench the emission.

The optimal concentration of Er^{3+} activator among the Gd_2O_3:Er (0.25-8%) series is 1%. Nanoparticles with such dopant amount have a larger barrier for luminescence quenching and, as a result, the highest quantum efficiency. These recommendations are the basis for further searching the ways to tunable and improve the characteristics of energy conversion devices on the basis of Gd_2O_3:Er system.

Acknowledgments

The work has been funded by the Ministry of Education and Science of the Russian Federation (Government task №3.1485.2017/4.6).

References

[1] Zatsepin A F, Kuznetsova Yu. A. 2015 *J. Phys. Conf. Ser.* **643** 012057
[2] Kuznetsova Yu A, Zatsepin A F, Pustovarov V A et all 2017 *J. Phys. Conf. Ser.* **917** 052015
[3] Trofimova E S, Pustovarov V A, Zatsepin A F 2017 *AIP Conf. Proc.* **1886** 020024
[4] Zatsepin D A, Boukhvalov D W, Zatsepin A F et all 2018 *Appl. Surf. Sci.* **436** 697-707
[5] Zatsepin A F, Kuznetsova Yu A, Spallino L et all 2016 *Energy Proc.* **102** 144-151
[6] Bünzli J-C G, Eliseeva S B 2010 *Basics of Lanthanide Photophysics* (Springer, Berlin)
[7] Zatsepin A F, Kuznetsova Yu A 2018 *Appl. Mater. Today* **12** 34-42
[8] Zatsepin A F, Kuznetsova Yu A et all 2018 *Iop Conf. Ser.: Mat. Sci. Eng.* **292** 012047